



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

XPS Investigation on Changes in UO₂ Speciation following Exposure to Humidity

S. B. Donald, M. L. Davisson, A. J. Nelson

March 14, 2016

2016 MRS Spring Meeting & Exhibit
Phoenix, AZ, United States
March 28, 2016 through April 1, 2016

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

XPS Investigation on Changes in UO_2 Speciation following Exposure to Humidity

Scott B. Donald, M. Lee Davisson, Art J. Nelson
Lawrence Livermore National Laboratory, Livermore, CA 94550, U.S.A.

ABSTRACT

High purity UO_2 powder samples were subjected to accelerated aging under controlled conditions with relative humidity ranging from 34% to 98%. Characterization of the chemical speciation of the products was accomplished using X-ray photoelectron spectroscopy (XPS). A shift to higher uranium oxidation states was found to be directly correlated to increased relative humidity exposure. Additionally, the relative abundance of O^{2-} , OH , and H_2O was found to vary with exposure time. It is thus expected that uranium oxide materials exposed to high relative humidity conditions during processing and storage would display a similar increase in average uranium valence.

INTRODUCTION

Under ambient conditions, U_3O_8 is the most stable compound in the U-O system [1]. The initial step in the oxidation of uranium dioxide (UO_2) in a wet environment is the adsorption of water on the surface of the material. While most DFT calculations suggest water non-dissociatively adsorbs on low-index surfaces, high defect surfaces are predicted to adsorb water in a dissociative manner, yielding H^+ , OH^- , and O^{2-} [2-7]. Experimentally, even at low temperatures, UO_2 oxidizes when exposed to air [8,9], initially yielding U_4O_9 and U_3O_7 through incorporation of adventitious oxygen in the fluorite structure. Oxidation in this regime is diffusion-controlled, yielding an oxidation front with a characteristic oxygen penetration rate. The subsequent formation of U_3O_8 in this oxidized region entails a more extensive structural rearrangement and involves nucleation and growth kinetics, yielding a comparatively sluggish transformation. In the presence of significant quantities of water (*i.e.*, a high relative humidity) various hydrates, hydroxides, and carbonates can form during the oxidation process [9].

Due to the kinetics of oxygen adsorption and penetration into UO_2 surfaces, oxidation is typically confined to the near-surface region. X-ray photoelectron spectroscopy (XPS) has been used previously to identify oxidation state of uranium on the UO_2 surface, indicating the extent to which it has been oxidized [10], as well as the presence and ratios of O^{2-} , OH^- , and H_2O groups in the O 1s spectra to provide insight into dissociative adsorption processes at work [11-14]. While studies have been performed measuring the structure and extent of oxidation following exposure to a range of environmental conditions, there currently exists no generalized model for the prediction of oxidized layer growth as a function of time, relative humidity, and oxygen concentration. In this study, UO_2 powders were aged under controlled conditions and the oxidation progress was monitored as a function of relative humidity and exposure time using X-ray photoelectron spectroscopy.

EXPERIMENTAL DETAILS

Samples of stoichiometric UO_2 were exposed individually to relative humidity ranging from 34% to 98%, as detailed in Table I, for a period of one, three, six, and nine months to the

humidity and 20% O₂. The relative humidity of the samples was controlled by placing inorganic salt slurries into a vacuum desiccator, which was then allowed to equilibrate to a fixed value inside the vessel and monitored with an internal hygrometer. Aliquots of these samples were then dispensed in room air and loaded in a HEPA-filtered hood onto carbon sticky tape mounted to an XPS sample holder. During the short transfer time of the sample from the controlled conditions of the desiccator to the vacuum chamber, the exposure to relative humidity of room air (~30%) should not have a discernable impact on the stoichiometry of the samples.

Table I. Initial Exposure Conditions for Stoichiometric UO₂

Salt Slurry	Relative Humidity
98% CaCl · 6 H ₂ O	34%
99% Mg(NO ₃) ₂ · 6 H ₂ O	55%
99% K ₂ SO ₄	98%

X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantum 2000 system using a focused, mono-chromatic Al K α X-ray (1486.7 eV) source for excitation and a spherical section analyzer. A 200 μ m diameter X-ray beam incident to the surface normal was used for analysis with the detector set at 45° from the surface normal. Spectra were collected using a pass energy of 23.5 eV, giving an energy resolution of 0.3 eV, that when combined with the 0.85 eV full width at half maximum (FWHM) Al K α line width gives a resolvable XPS peak width of 1.2 eV. Deconvolution of unresolved, core-level peaks was accomplished using MultiPak 9.6 (PHI) curve fitting routines with asymmetric or Gaussian-Lorentzian line shapes and a Shirley background. Low energy electrons were used for specimen charge neutralization. The collected data were referenced to an energy scale with binding energies for Cu 2p_{3/2} at 932.72 \pm 0.05 eV and Au 4f_{7/2} at 84.01 \pm 0.05 eV. Binding energies were also referenced to the C 1s photoelectron line arising from adventitious carbon at 284.8 eV. Low energy electrons were used for specimen neutralization.

DISCUSSION

Figure 1 presents the mean uranium valence as calculated from the U 4f_{7/2,5/2} core-level spectra for the aged UO₂ powders as a function of relative humidity and exposure time. Curve fitting of the U 4f_{7/2,5/2} spin-orbit pair for the aged samples revealed three 4f_{7/2} components at 380.0 eV, 380.8 eV, and 381.7 eV indicative of U⁴⁺, U⁵⁺, and U⁶⁺ respectively [11,14]. The mean uranium valence increased with exposure to higher relative humidity as well as for longer exposure durations; however greater change in the mean uranium valence was seen as a function of time as compared to relative humidity. While the mean uranium valence is ultimately limited to fully U⁶⁺, the variation in mean uranium valence appears to decrease with time prior to reaching this limit. This is perhaps an indication of a change in the predominant mechanism for the samples as they oxidized from UO₂ to U₄O₉, U₃O₈, and other species.

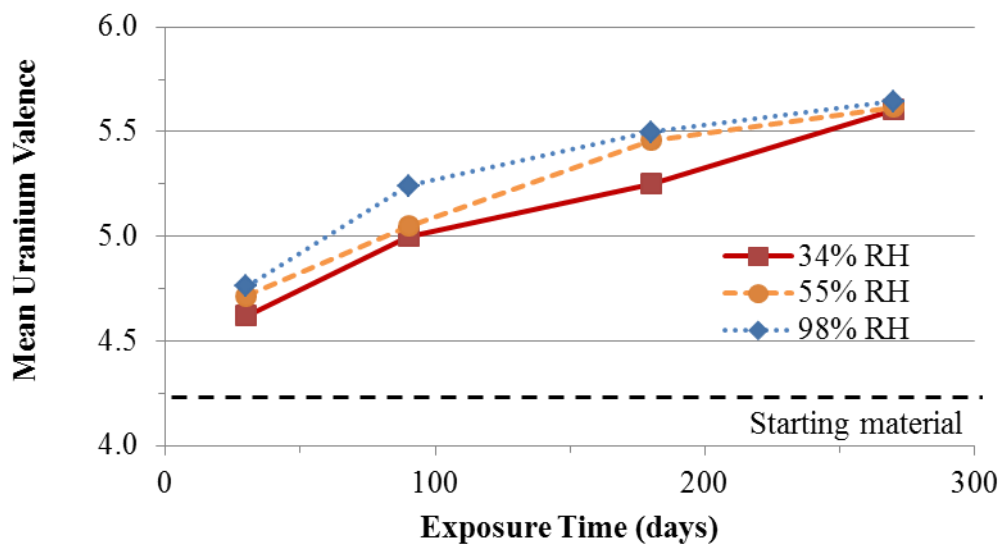


Figure 1. Mean uranium valence as a function of exposure time and relative humidity from XPS analysis of the U4f peaks

The O 1s core-level spectra for the UO_2 samples aged for 90 days as a function of relative humidity are presented in Figure 2. The O 1s structure is dominated by an oxide peak at 530.2 eV for the sample aged at 34% relative humidity, which shifts to higher binding energies for samples exposed to higher relative humidity, ultimately positioned at 531.4 eV for the sample aged at 98% relative humidity. This shift is consistent with that seen for increasingly oxidized uranium species and is in agreement with the variation in the mean uranium valence described previously. The samples aged at 55% and 98% relative humidity also presented a lower binding energy shoulder at 529.8 eV, which upon peak fitting is revealed as a U-O-U peak relating to “ O^{2-} in the equatorial plane of the uranium polyhedral” [12].

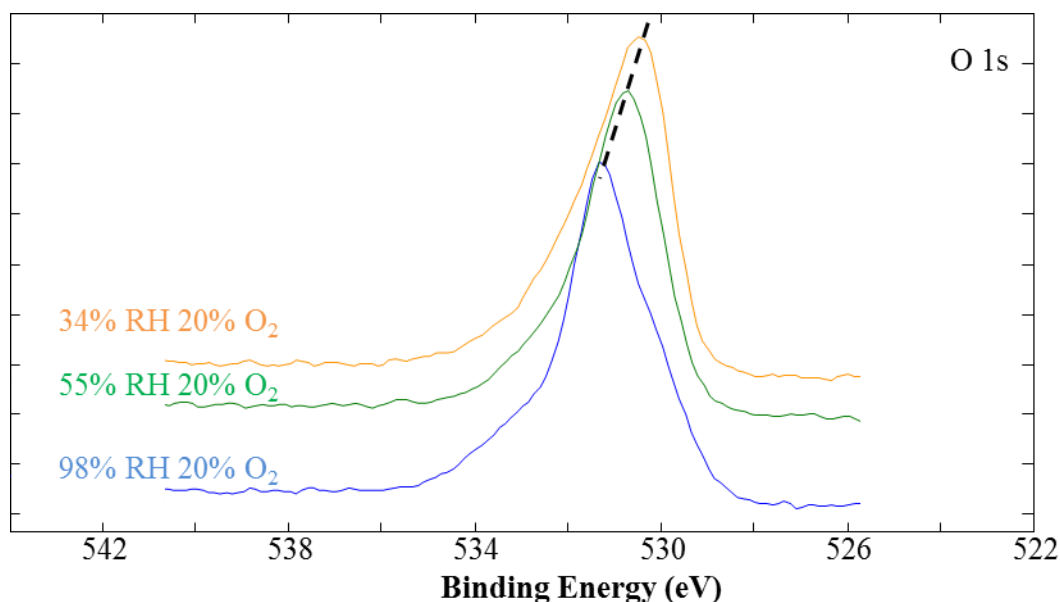


Figure 2. XPS O 1s spectra of the UO_2 samples aged for 90 days

The percent of the O 1s spectra as component peaks as a function of exposure to 55% relative humidity and 20% O₂ are illustrated in Figure 3. The intensity of the slight U-O-U shoulder seen at 90 days was found to grow in intensity for the 180 and 270 day samples. The relative concentration of the H₂O to OH peak areas decreased between the 30, 90, and 180 day samples but appears to increase slightly between the 180 and 270 day samples. Interestingly, the H₂O and OH peak areas have an approximate ratio of 1:3 for all samples taken during the exposure series. Future work will work to elucidate if the ratios of O²⁻, OH, and H₂O provide insight into the current oxidation state of the uranium as well as the dissociative mechanisms at work.

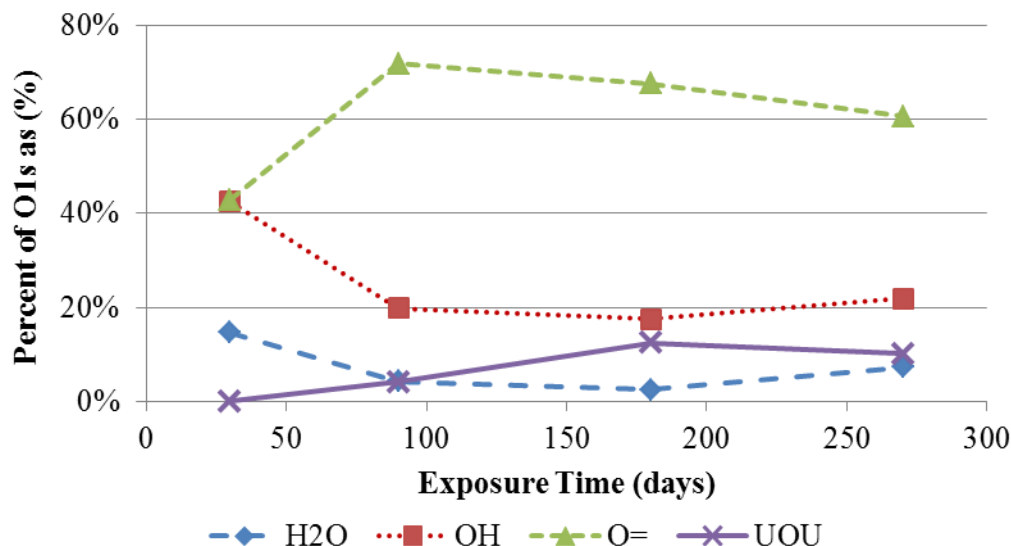


Figure 3. Variation in oxygen speciation from XPS analysis of the O1s peak with exposure to 55% relative humidity and 20% O₂

CONCLUSIONS

Stoichiometric samples of uranium dioxide powder were exposed to relative humidity ranging from 34% to 98%, controlled by varying saturated inorganic salt slurries, and 20% O₂. Samples were taken at 30, 90, 180, and 270 days and the oxidation of each was compared using X-ray photoelectron spectroscopy. The mean valence of uranium was found to increase with time for all relative humidities, progressing most quickly for the sample exposed to 98% relative humidity. For the UO₂ powders exposed for 90 days, a systematic increase in O1s binding energy was observed with increasing relative humidity, in agreement with the increased oxidation of the samples. Oxygen speciation was found to vary over exposure time, with the relative concentration of oxide (O=) increasing and hydroxyl (OH-) decreasing drastically from samples drawn at 30 to 90 days.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

REFERENCES

1. Desgranges L., G. Baldinozzi, G. Rousseau, J.C. Nièpce, G. Calvarin, *Inorg. Chem.* **48** (2009) 7585.
2. Alexandrov V., T.Y. Shvareva, S. Hayun, M. Asta, A. Navrotsky, *J. Phys. Chem. Lett.* **2** (2011) 3130.
3. Bo T., J.H. Lan, Y.L. Zhao, Y.J. Zhang, C.H. He, Z.F. Chai, W.-Q. Shi, *J. Nucl. Mater.* **454** (2014) 446.
4. Hay P.J., *Mater. Res. Soc. Symp. Proc.* **893** (2006).
5. Maldonado P., L.Z. Evins, P.M. Oppeneer, *J. Phys. Chem. C* **118** (2014) 8491.
6. Tian X., H. Wang, H. Xiao, T. Gao, *Comput. Mater. Sci.* **91** (2014) 364.
7. Weck P.F., E. Kim, C.F. Jové-Colón, D.C. Sassani, *Dalt. Trans.* **42** (2013) 4570.
8. Rousseau G., L. Desgranges, F. Charlot, N. Millot, J.C. Nièpce, M. Pijolat, F. Valdivieso, G. Baldinozzi, J.F. Béar, *J. Nucl. Mater.* **355** (2006) 10.
9. McEachern R.J., P. Taylor, *J. Nucl. Mater.* **254** (1998) 87.
10. Ilton E.S., P.S. Bagus, *Surf. Interface Anal.* **43** (2011) 1549.
11. Idriss H., *Surf. Sci. Rep.* **65** (2010) 67.
12. Schindler M., F.C. Hawthorne, M.S. Freund, P.C. Burns, *Geochim. Cosmochim. Acta* **73** (2009) 2488.
13. Senanayake S.D., G.I.N. Waterhouse, A.S.Y. Chan, T.E. Madey, D.R. Mullins, H. Idriss, *Catal. Today* **120** (2007) 151.
14. K.S. Holliday, W. Siekhaus and A.J. Nelson, *J. Vac. Sci. Technol. A* **31**, 031401 (2013).